

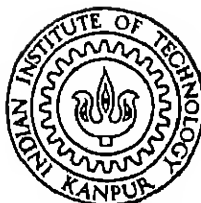
# MODELLING OF SELECTIVE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE ON VPO CATALYSTS

by

UPENDRA CHANDRA JOSHI

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DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
DECEMBER, 1989

# **MODELLING OF SELECTIVE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE ON VPO CATALYSTS**

*A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of*  
**MASTER OF TECHNOLOGY**

*by*  
**UPENDRA CHANDRA JOSHI**

*to the*  
**DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
DECEMBER, 1989**

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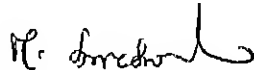
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CERTIFICATE

This is to certify that the present work entitled "MODELLING OF SELECTIVE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE ON VPO CATALYSTS" has been carried out by Upendra Chandra Joshi, under my supervision and it has not been submitted elsewhere for a degree.

  
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DECEMBER, 1989

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Upendra Chandra Joshi

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# NOMENCLATURE

B	n-butane
C	Oxides of Carbon
E	Activation energy
F	Flow rate of reactants
$F_{Bo}$	Flow rate of n-butane in the feed
k	Rate constants
MA	Maleic anhydride
m	Order of reaction with respect to butane
n	order of reaction with respect to oxygen
$p_o$	Partial pressure of oxygen
$p_{MA}$	Partial pressure of maleic anhydride
$p_B$	Partial pressure of n-butane
$p_C$	Partial pressure of oxides of carbon
r	Order of reaction with respect to n-butane
$-r_B$	Rate of consumption of n-butane
$r_C$	Rate of production of oxides of carbon
$r_{MA}$	Rate of production of maleic anhydride

s	Order of reaction with respect to maleic anhydride
T	Temperature
W	Mass of catalyst bed
X	Conversion of n-butane
Y	Yield of maleic anhydride
Z	Yield of maleic anhydride
$\alpha, \beta, \gamma$	Stoichiometric coefficients
$\theta_R$	Fraction of reduced sites
$\theta_{O_2}$	Fraction of oxidized sites

## SYNOPSIS

Maleic anhydride is an industrially important chemical. It can be produced from oxidation of benzene. Now-a-days its production from  $C_4$ - hydrocarbon has gained considerable significance. The most widely used catalyst for this reaction is Vanadium- Phosphorous Oxides (VPO).

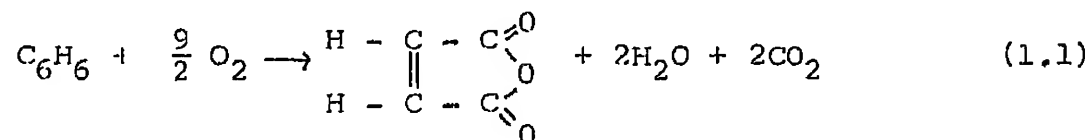
In the present work the kinetics of the reaction in an integral tubular reactor, data of which are available in literature, has been modelled. Various studies have shown that the reaction takes place via a redox mechanism. A model based on redox mechanism has been investigated. Using the experimental data of Gopichand (1) various kinetic parameters involved in the reaction model has been estimated and the plausibility of the proposed model has been discussed. A few other models (1), (4) have also been used to estimate the various kinetic parameters.

## CHAPTER 1

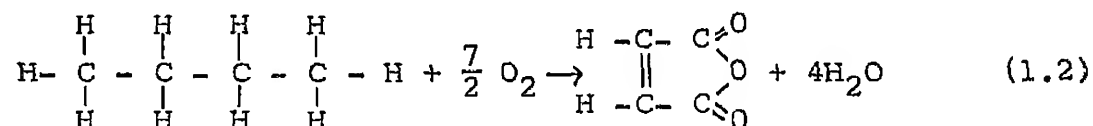
### INTRODUCTION

Maleic anhydride and its derivatives are produced world-wide. This industrially important chemical is used in the production of agricultural chemicals, resins, food additives, lubricating oil additives and pharmaceuticals.

Earlier benzene was oxidized to produce maleic anhydride. The reaction can be represented by



Now-a-days benzene is being replaced by  $\text{C}_4$ -hydrocarbon as the feed stock. n-Butane feed is generally preferred because of its low cost and further more it is <sup>an</sup>environmentally more desirable raw material. The catalytic oxidation of butane produces a product stream which mainly contains <sup>of</sup> maleic anhydride and carbon oxides. The reaction can be represented by



Vanadium Phosphorous Oxide (VPO) system is generally used as the catalyst for the production of maleic anhydride from n-butane. In this catalyst, many phases may exist, for example, Vanadium may show oxidation states like V(III), V(IV), V(V) etc. The presence of various phases depend on many synthesis variables. The catalytic composition and method of preparation were found to be important parameters for the reaction.

In order to understand a catalytic reaction, kinetic modelling becomes an important task. In simple terms, modelling is to build a mathematical model for the system through which it becomes possible to predict, control and optimize the system. The modelling of a system is a very involved task. It starts with assuming certain plausible models and then estimating the parameters appearing in the model with the available experimental data. Next step is to discriminate among the rival models and finally check the adequacy of the model thus proposed.

For the present study, the experimental data were taken from literature (1). These data were taken for a continuous reactor. The feed stream consisted of n-butane and air which after compression and preheating was passed to the reactor. The conversion and yields were large enough, so that an integral

analysis was possible experiments were conducted in such a way that external and intrapellet mass transfer and heat transfer resistances were negligible. This is important because in order to determine kinetic parameters, data are required which are unmasked by transport resistances.

The Vanadium -Phosphorous Oxide (VPO) catalyst used by Gopichand (1) had the following composition:

$V_2 O_5$	=	15.3%
$P_2 O_5$	=	9.7 %
Fe	=	0.5%
Silica gel	=	74.8%

The aim of the present work was to model the selective oxidation of n-butane to maleic anhydride using Gopichand's data.

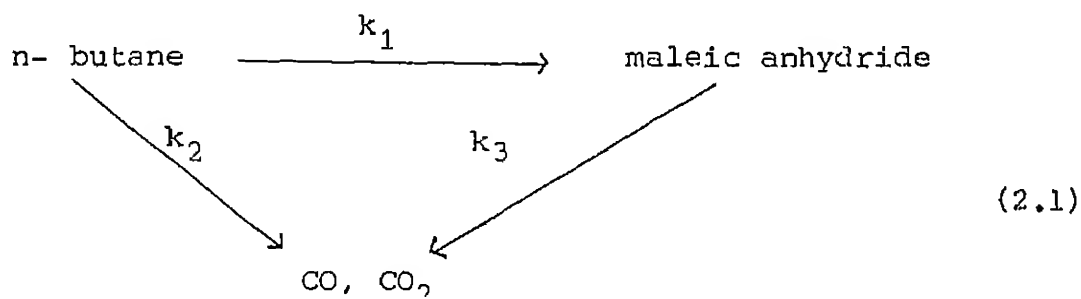


## CHAPTER 2

### STUDIES ON THE KINETICS AND MECHANISM OF C<sub>4</sub>-HYDROCARBON ON VPO CATALYST

#### 2.1 INTRODUCTION

The kinetics of the n-butane oxidation on vanadium phosphorous mixed oxides has been studied by Escardino et-al, (2), and by Wohlfahrt and Hofman (3), among others. The reaction scheme proposed was



It was found that at a low hydrocarbon partial pressure, the behaviour of n-butane oxidation may be described by three single pseudo-first order rate expressions. Oxygen chemisorption was found as the rate determining step at large butane pressures.

Wohlfahrt and Hofmann studied the reaction using a catalyst with a P/V ratio of 1.06, and extended the range of hydrocarbon and oxygen concentrations investigated by Escardino et-al (2) and found

that n-butane is oxidized according to a rate equation of the type

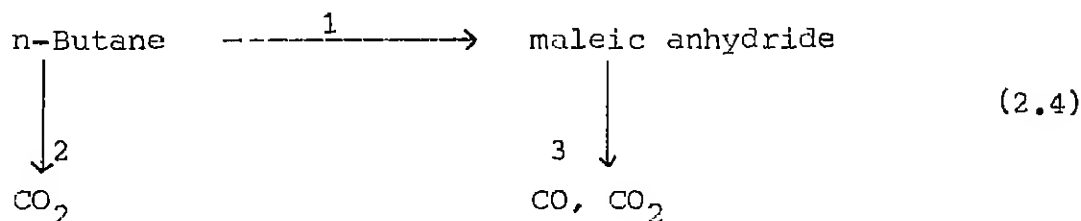
$$r_B = \frac{k p_B p_O^{0.285}}{1 + k p_B} \quad (2.2)$$

and maleic anhydride is oxidized according to a rate equation of the type

$$r_{MA} = \frac{k p_{MA} p_O^{0.285}}{1 + k p_B} \quad (2.3)$$

Where the subscripts B, o and MA designate butane, oxygen and maleic anhydride respectively.

Another study by centi-et-al (4) gives a different reaction scheme. This is given by



Rate equations of the following type were proposed by centi-et-al. (4).

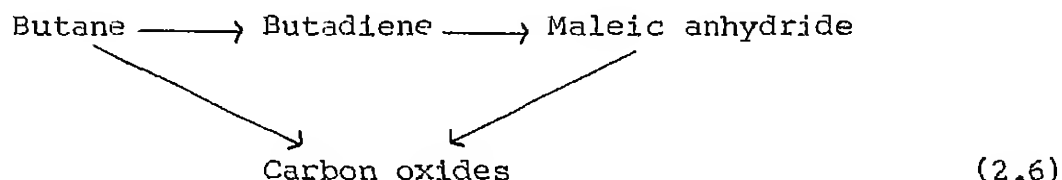
$$\begin{aligned}
 r_1 &= \frac{k_1 k_B p_B p_O^a}{(1 + k_B p_B)} \\
 r_2 &= k_2 p_O^b
 \end{aligned} \quad (2.5)$$

$$r_3 = k_3 p_{MA} \frac{p_o^e}{p_B^b}$$

Where  $r_1$  is the rate of formation of maleic anhydride

$r_2$  is the rate of formation of Carbon dioxide and  $r_3$  is the rate of the decomposition of the maleic anhydride.

A redox mechanism has been proposed by Mars and Van Krevelen (5). Varma and Saraf (6) also used a redox model to fit their data for the oxidation of n-butane to maleic anhydride on a VPO catalyst. Butadiene was found to be a major intermediate in the proposed reaction scheme-



pseudo first order rate expressions were fitted to each of the above reaction steps at low hydrocarbon concentrations.

A study by Cavani-et-al (7) has shown that 1-butane adsorbed on a V(IV) site oxidizes to butadiene accompanying the formation of V(III) site. If the concentration of V(V) sites around the adsorbed butadiene is high enough, butadiene is further oxidized to maleic anhydride or carbon oxides. On the other hand if the concentration of V(V) sites is low, butadiene desorbs from the V(III) site.

In the case of n-butane, when the concentration of n-butane is low, intermediates such as butene and butadiene were not detected. Only at high concentration of n-butane, butene and butadiene were detected.

A redox model for the oxidation of n-butane has been proposed by Gopichand (1). He proposed that when n-butane adsorbs on V(IV) site, it is converted to olefins and V(III) forms. If the density of the oxidized sites V(V) in the vicinity of the adsorbed olefins is high, these olefins are further oxidized to maleic anhydride. But if the density of the V(V) sites is low, the olefins desorb.

The proposed rate expressions are

$$-r_B = \frac{k_1 p_{O_2} + k_3 p_B}{\left(1 + \frac{k_1 p_{O_2}}{k_2 p_B} + \frac{k_3 p_B}{k_5 p_{O_2}} + \frac{k_4 p_{MA}}{k_5 p_{O_2}}\right)} \quad (2.7)$$

$$r_{MA} = \frac{k_1 p_{O_2} - k_4 p_{MA}}{\left(1 + \frac{k_1 p_{O_2}}{k_2 p_B} + \frac{k_3 p_B}{k_5 p_{O_2}} + \frac{k_4 p_{MA}}{k_5 p_{O_2}}\right)} \quad (2.8)$$

$$r_C = \frac{k_3 p_B + k_4 p_{MA}}{\left(1 + \frac{k_1 p_{O_2}}{k_2 p_B} + \frac{k_3 p_B}{k_5 p_{O_2}} + \frac{k_4 p_{MA}}{k_5 p_{O_2}}\right)} \quad (2.9)$$

Where  $r_B$  is the rate of reaction of n-butane.

$r_C$  is the rate of production of oxides of carbon and

$r_{MA}$  is the rate of production of maleic anhydride.

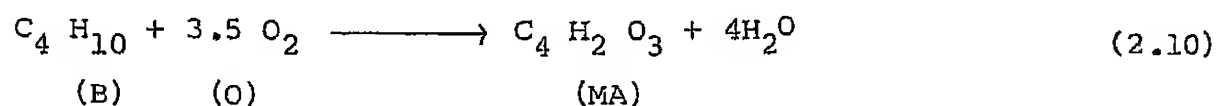
Gopichand (1) obtained the data using two VPO catalysts with and without iron promoter, using a P/V atomic ratio of 1.20. The catalyst had a surface area of  $58 \text{ m}^2/\text{gm}$ . The data for promoted catalyst in the temperature range of  $350^\circ\text{C} - 400^\circ\text{C}$  were used in the present investigation for modelling. The data used are given in Appendix 1.

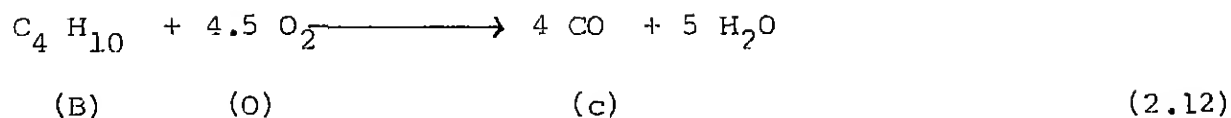
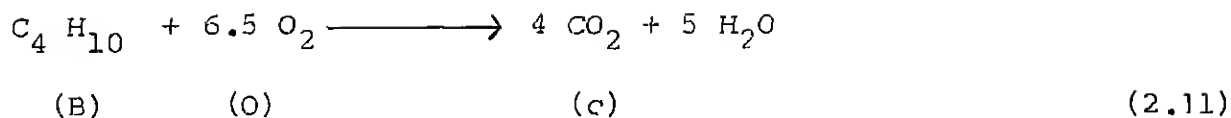
## 2.2 SOME GENERAL CONSIDERATIONS

The analysis is possible either by an integral method or by a differential method. Since the data were available for an integral reactor (i.e. high conversion and yields), an integral analysis had been used.

The details of the kinetic model proposed by Gopichand as well as other models, tested in the present investigation are given in Section 2.3 and 2.4.

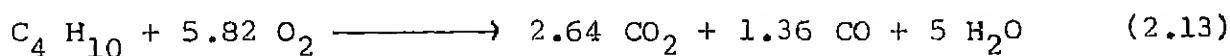
The reactions involved in the selective oxidation of n-butane are as follows-





The experimental conditions are such that the ratio of the rate of formation of  $\text{CO}_2$  to the rate of formation of  $\text{CO}$  is 1.942.

Hence on the average the reaction for carbon oxide formation can be written as



This equation can be obtained from Equations (2.11) and (2.12).

The partial pressure of butane, maleic anhydride and oxides of carbon ( $p_B$ ,  $p_{MA}$ ,  $p_C$ ) can be expressed in terms of conversion and yields as follows-

Conversion  $X$  of n-butane is given by

$$X = \frac{p_{B_0} - p_B}{p_{B_0}} = \frac{\text{mol of n-butane converted}}{\text{mol of n-butane fed}}$$

$$\therefore p_B = p_{B_0} (1 - X) \quad (2.14)$$

yield of maleic anhydride

$$y = \frac{\text{mol of maleic anhydride formed}}{\text{mol of n-butane fed}}$$

$$= \frac{p_{MA}}{p_{Bo}}$$

$$\text{so } p_{MA} = p_{Bo} y \quad (2.15)$$

yield of oxides of carbon

$$z = \frac{\text{mol of oxides of carbon formed}}{\text{mol of butane fed}}$$

$$= \frac{p_C}{4p_{Bo}}$$

$$\text{so } p_C = (4) (z) p_{Bo} \quad (2.16)$$

Equations (2.10) and (2.13) can be used to find partial pressure of oxygen. Let at any point in the reactor, partial pressure of maleic anhydride and oxides of carbon be  $p_{MA}$  and  $p_C$ .

Then due to formation of maleic anhydride, the partial pressure of oxygen reduces by  $3.5 p_{MA}$  (from Equation (2.10)) and due to formation of oxides of carbon, the partial pressure of  $O_2$  reduces by  $\frac{5.82}{4.00} p_C$  (from Equation (2.13)) so the partial pressure

of oxygen can be written as

$$p_{O_2} = p_{O_2}^O - 3.5 p_{MA} - \frac{5.82}{4.0} p_C \quad (2.17)$$

Where  $p_{O_2}^O$  is partial pressure of oxygen in feed stream.

Now on substituting  $p_{MA}$  and  $p_C$  (from Equations (2.15) and (2.16)) in Equation (2.17), we get partial pressure of oxygen in terms of conversion and yields as

$$p_{O_2} = p_{O_2}^O - 3.5 p_{Bo} y - 5.82 p_{Bo} z \quad (2.18)$$

Equations (2.14), (2.15), (2.16) and (2.18), assumes that there is no volume change during the reaction. This is valid since the partial pressure of n-butane in the feed is very low and a large amount of inert (nitrogen) is present in the feed.

We can also write continuity equations for n-butane, maleic anhydride and carbon oxides for the isothermal fixed bed reactor.

Consider an element of length 'dl' in the reactor

Input of butane =  $F_B$

Output of butane =  $(F_B + dF_B)$

Disappearance of butane by reaction

$$= (-r_B) (dW)$$

Where  $(-r_B)$  the mol of butane reacted per sec. per unit mass of the catalyst.



Now the continuity equation is

Input = Output + disappearance by reaction + accumulation

at steady state, there is no accumulation

Hence  $F_B = (F_B + dF_B) + (-r_B) (dW)$

$$dF_B + (-r_B) (dW) = 0 \quad (2.19)$$

Now conversion is defined by the equation

$$F_B = F_{B0} (1 - x)$$

so  $dF_B = d(F_{B0} (1 - x)) = -F_{B0} dx$

using this equation in (2.19)

$$-F_{B0} dx + (-r_B) dW = 0$$

$$F_{B0} dx = (-r_B) dW$$

$$\frac{dx}{d(W/F_{B0})} = (-r_B) \quad (2.20)$$

Similarly for maleic anhydride formation, continuity equation is

$$\frac{dy}{d(W/F_{B0})} = r_{MA} \quad (2.21)$$

and for oxides of carbon, the continuity equation is

$$\frac{dz}{d(W/F_{B0})} = r_C \quad (2.22)$$

In order to solve the continuity equations (2.20), (2.21) and (2.22) we need rate expressions. These rate expressions have been obtained from various models proposed for the reaction. The solution of these equations give values of conversion and yields and these can be used to obtain various parameters involved in the reaction kinetics. Parameter estimation involves minimization of residual sum of squares.

The initial conditions needed to solve the equations are

$$x = 0$$

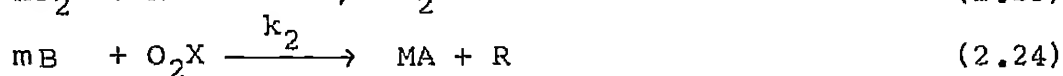
$$y = 0 \quad \text{at} \quad \frac{W}{F_{Bo}} = 0 \quad (2.22a)$$

$$z = 0$$

### 2.3 MODEL 1 (REDOX MODEL)

The selective oxidation reactions on oxide catalysts are assumed to follow redox mechanism. Gopichand (1) has proposed a kinetic model based on redox concept involving three types of active catalytic sites with different oxidation states.

Various steps in the redox mechanism are as follows-



Where

B is butane

MA is maleic anhydride

C is oxides of carbon

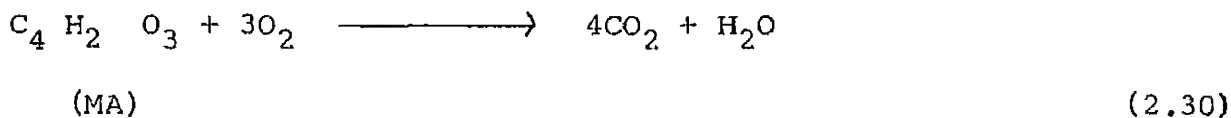
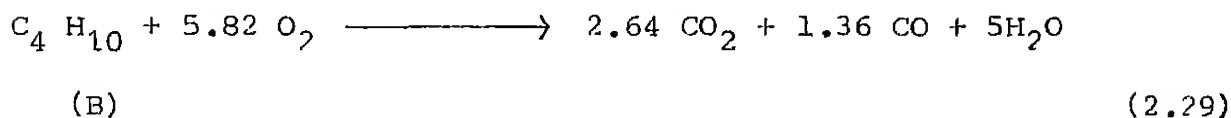
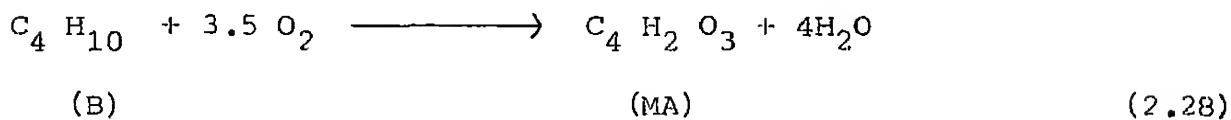
R is reduced site

F is further reduced site and

O<sub>2</sub>x is an oxidized site

n, m, r and s are orders of reaction with respect to oxygen, butane and maleic anhydride in Equations (2.23), (2.24), (2.26) and (2.27) respectively.

Various overall reactions are



At steady state, the net rates of production of sites O<sub>2</sub>X, R and F are equal to zero.

From Equations (2.23), (2.24) and (2.28), we can write-

Oxygen balance on site  $O_2 X$

$$k_1 p_{O_2}^n \theta_R = \alpha k_2 p_B^m \theta_{O_2 X} \quad (2.31)$$

Similarly, oxygen balance on site R (using Equations 2.23 to 2.30)

$$\begin{aligned} k_1 p_{O_2}^n \theta_R + \beta k_3 p_B^r \theta_R + \gamma k_4 p_{MA}^s \theta_R \\ = \alpha k_2 p_B^m \theta_X + k_5 p_{O_2}^n (1 - \theta_R - \theta_{O_2 X}) \end{aligned}$$

Using (2.31) in the above equation

$$\beta k_3 p_B^r \theta_R + \gamma k_4 p_{MA}^s \theta_R = k_5 p_{O_2}^n (1 - \theta_R - \theta_{O_2 X}) \quad (2.32)$$

put the value of  $\theta_{O_2 X}$  from (2.31) in Equation (2.32)

$$\begin{aligned} \beta k_3 p_B^r \theta_R + \gamma k_4 p_{MA}^s \theta_R + k_5 p_{O_2}^n \theta_R &= k_5 p_{O_2}^n \left( 1 - \frac{k_1 p_{O_2}^n \theta_R}{\alpha k_2 p_B^m} \right) \\ \theta_R \left( \beta k_3 p_B^r + \gamma k_4 p_{MA}^s + k_5 p_{O_2}^n + \frac{k_1 k_5 p_{O_2}^n p_{O_2}^n}{\alpha k_2 p_B^m} \right) &= k_5 p_{O_2}^n \\ \theta_R &= \frac{k_5 p_{O_2}^n}{\left( \beta k_3 p_B^r + \gamma k_4 p_{MA}^s + k_5 p_{O_2}^n + k_5 p_{O_2}^n \frac{k_1 p_{O_2}^n}{\alpha k_2 p_B^m} \right)} \end{aligned}$$

$$\theta_R = \frac{1}{(1 + \frac{k_1 p_{O_2}^n}{\alpha k_2 p_B^m} + \frac{\beta k_3 p_B^r}{k_5 p_{O_2}^n} + \frac{\gamma k_4 p_{MA}^s}{k_5 p_{O_2}^n})} \quad (2.33)$$

In the above equations,  $\alpha$ ,  $\beta$  and  $\gamma$  are stoichiometric coefficients. From Equation (2.28)  $\alpha$  is equal to 3.5, from Equation (2.29)  $\beta$  is equal to 5.82 and from Equation (2.30)  $\gamma$  is equal to 3.0.

Now, from Equations (2.24) and (2.25), the rate of depletion of n-butane can be written as

$$-r_B = k_2 p_B^m \theta_{O_2^x} + k_3 p_B^r \theta_R$$

Using Equation (2.31) for  $\theta_{O_2^x}$

$$-r_B = k_2 p_B^m \frac{k_1 p_{O_2}^n}{\alpha k_2 p_B^m} \theta_R + k_3 p_B^r \theta_R$$

$$-r_B = \left( \frac{k_1 p_{O_2}^n}{\alpha} + k_3 p_B^r \right) \theta_R$$

Using the value of  $\theta_R$  from Eqn. (2.33) in the above expression, we get

$$-r_B = \left( \frac{k_1 p_{O_2}^n}{\alpha} + k_3 p_B^r \right) \frac{1}{(1 + \frac{k_1 p_{O_2}^n}{\alpha k_2 p_B^m} + \frac{\beta k_3 p_B^r}{k_5 p_{O_2}^n} + \frac{\gamma k_4 p_{MA}^s}{k_5 p_{O_2}^n})}$$

or

$$-r_B = \frac{k'_1 p_{O_2}^n + k_3 p_B^r}{\left( 1 + \frac{k'_1 p_{O_2}^n}{k_2 p_B^m} + \frac{k'_3 p_B^r}{k_5 p_{O_2}^n} + \frac{k'_4 p_{MA}^s}{k_5 p_{O_2}^m} \right)} \quad (2.34)$$

$$\text{Where } k'_1 = \frac{k_1}{\alpha}$$

$$k'_3 = \beta k_3 \text{ and}$$

$$k'_4 = \gamma k_4$$

From Equations (2.24) and (2.26), the rate of formation of maleic anhydride can be written as

$$r_{MA} = k_2 p_B^m \theta_{O_2 x} - k_4 p_{MA}^s \theta_R$$

Using Equation (2.31) for  $\theta_{O_2 x}$

$$\begin{aligned} r_{MA} &= k_2 p_B^m \frac{k_1 p_{O_2}^n}{\alpha k_2 p_B^m} \theta_R - k_4 p_{MA}^s \theta_R \\ &= \left( \frac{k_1 p_{O_2}^n}{\alpha} - k_4 p_{MA}^s \right) \theta_R \end{aligned}$$

using Equation (2.33) for  $\theta_R$

$$= \left( \frac{k_1 p_{O_2}^n}{\alpha} - k_4 p_{MA}^s \right) \frac{1}{\left( 1 + \frac{k_1 p_{O_2}^n}{\alpha k_2 p_B^n} + \frac{\beta k_3 p_B^r}{k_5 p_{O_2}^n} + \frac{\gamma k_4 p_{MA}^s}{k_5 p_{O_2}^n} \right)}$$

So,

$$r_{MA} = \frac{k_1' p_{O_2}^n - k_4 p_{MA}^s}{\left( 1 + \frac{k_1' p_{O_2}^n}{k_2 p_B^m} + \frac{k_3' p_B^r}{k_5 p_{O_2}^n} + \frac{k_4' p_{MA}^s}{k_5 p_{O_2}^n} \right)} \quad (2.35)$$

From Equations (2.25) and (2.26), the rate of formation of oxides of carbon can be written as

$$r_c = k_3 p_B^r \theta_R + k_4 p_{MA}^s \theta_R$$

Using Equation (2.33) for  $\theta_R$

$$\begin{aligned} r_c &= (k_3 p_B^r + k_4 p_{MA}^s) \frac{1}{\left( 1 + \frac{k_1 p_{O_2}^n}{\alpha k_2 p_B^m} + \frac{\beta k_3 p_B^r}{k_5 p_{O_2}^n} + \frac{\gamma k_4 p_{MA}^s}{k_5 p_{O_2}^n} \right)} \\ &= \frac{k_3 p_B^r + k_4 p_{MA}^s}{\left( 1 + \frac{k_1' p_{O_2}^n}{k_2 p_B^m} + \frac{k_3' p_B^r}{k_5 p_{O_2}^n} + \frac{k_4' p_{MA}^s}{k_5 p_{O_2}^n} \right)} \quad (2.36) \end{aligned}$$

The rate expressions (2.34), (2.35) and (2.36) can be expressed in terms of conversion of n-butane  $X$ , yield of maleic anhydride  $y$  and yield of carbon oxides  $z$ , using Equations (2.14), (2.15) and (2.18).

The resulting rate expressions in terms of conversion and yields are used to solve continuity Equations (2.20), (2.21) and (2.22).

Gopichand (1) assumed the reaction orders  $n$ ,  $m$ ,  $r$  and  $s$  involved in Equations (2.23), (2.24), (2.25) and (2.26) equal to one. Using this assumption, the rate expressions (2.34), (2.35) and (2.36) become same as proposed by Gopichand (1) and given by Equations (2.7), (2.8) and (2.9)

In the present investigation, parameter estimation has been done using Gopichand's model as well as above proposed general model which involves various reaction orders.

Since the oxygen present in the feed stream is in abundance the reaction order with respect to oxygen ' $n$ ' has been taken as zero

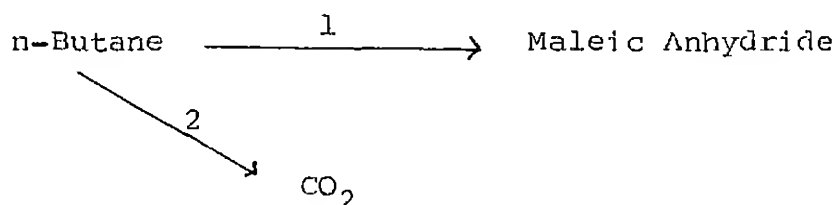
Also various investigations have shown that the order of reaction with respect to butane ' $m$ ' (Equation 2.24) is one. The order ' $r$ ' and ' $s$ ' in Equations (2.25) and (2.26) varies from 0.5 to 0.25.

Various combinations of ' $r$ ' and ' $s$ ' have been used in the parameter estimation. Details of the results are included in Chapter 4.



#### 2.4 MODEL 2 (CENTI'S MODEL)

Centi et-al (4) proposed a model for the reaction for conversion of the order of 10%. The reaction mechanism is

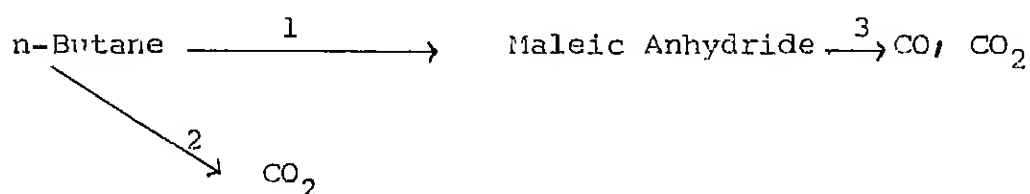


n-Butane is oxidized along two parallel routes. The first route, to maleic anhydride depends on the hydrocarbon concentration according to Langmuir Hinshelwood model, whereas the second route, to carbon dioxide does not depend on the hydrocarbon concentration. Increasing the n-butane concentration increases the selectivity in maleic Anhydride formation. Both reactions have slight dependence on the oxygen concentration, except at very low oxygen values, also the selectivity in maleic anhydride is constant in the range of experimented  $O_2$  concentrations. Their proposed equations are

$$r_1 = r_{ma} = \frac{k_1 k_B p_B (p_O)^a}{1 + k_B p_B} \quad (2.37)$$

$$r_2 = r_{CO_2} = k_2 (p_O)^b \quad (2.38)$$

But these equations were found to be inadequate when kinetic analysis was extended to integral conditions in the 0-100% conversion range. These equations were found to be adequate upto 60% conversion. For higher conversions, the experimental yields of maleic anhydride were lower than the calculated ones and for conversion of about 100%, the experimental yield of maleic anhydride is very low. Therefore a successive reaction of combustion of the maleic anhydride must occur. Parallel to the decrease in yield of maleic anhydride, a strong increase in the yields of both carbon mono and dioxides was found. In order to take these facts into account, the complete modified reaction model can be expressed as-



The rate expression for the 3<sup>rd</sup> reaction is

$$r_3 = r_{MA} = k_3 P_{MA} \frac{(p_O)^c}{(p_B)^d} \quad (2.39)$$

The rate equation of n-butane oxidation is

$$-r_B = r_{MA} + \frac{r_{CO_2}}{4} \quad (2.40)$$

## CHAPTER 3

### PARAMETER ESTIMATION

#### 3.1 INTRODUCTION

The experimental data of Gopichand have been used for modelling. The data at three different temperatures and various partial pressures of butane in the feedstream are given in Appendix 1. The data consisted of outlet yields and conversion at various W/F. The continuity Equations (2.20), (2.21) and (2.22) are also in terms of conversion and yields. For a given set of parameters, the solution of these continuity equations give values of conversion and yields at various W/F. These are calculated values based on a particular model. These values on subtraction from the experimental values give the deviations of calculated values from the experimental values. The purpose is to find a set of parameters which minimizes the objective function

$$F = \sum_{i=1}^N \left[ (x_{i_{\text{meas}}} - x_{i_{\text{cal}}})^2 + (y_{i_{\text{meas}}} - y_{i_{\text{cal}}})^2 + (z_{i_{\text{meas}}} - z_{i_{\text{cal}}})^2 \right] \quad (3.1)$$

Where 'i' indicates  $i^{\text{th}}$  experiment

- meas.    -    for experimental value
- calc.    -    for calculated value
- N        -    total number of experiments

This function  $F$  is to be minimized with respect to various parameters.

Several methods are available to minimize the function. Since these kinetic parameters can only have values greater than zero, the constrained minimization technique can also be employed. However, for the present study, unconstrained minimization method has been used.

The unconstrained methods can be classified into two broad categories as direct search methods and descent methods (8).

Generally the descent methods are more efficient compared to the direct search methods, but it requires, in addition to function evaluations, the evaluation of first and possibly higher order derivatives of the objective function  $F$ .

On the other hand, the direct search methods require only objective function evaluation and do not use the partial derivatives of the function.

Since in the present case, the exact functional relationship for conversion and yields in terms of kinetic parameters is not known, the derivative of the objective function with respect to parameters can not be calculated. So descent method, although desirable, can not be used.

For this reason, direct search method has been used for minimization of 'F'.

Among the various direct search methods available, it is the simplex method which is most accurate and efficient. So a simplex method has been used which is described in the following section.

### 3.2 SIMPLEX METHOD

Simplex is defined as a geometric figure formed by a set of  $(n+1)$  points in the  $n$ -dimensional space. For example, in a two dimensional space, the simplex is a triangle.

The basic idea in the simplex method is to compare the values of the objective function at the  $(n+1)$  vertices of a simplex and move this simplex gradually towards the optimum point during the iterative process. The movement of the simplex is achieved by using three operations known as reflection, contraction and expansion. The details of the method are given in Appendix 2.

### 3.3 SOLUTION OF DIFFERENTIAL EQUATIONS

The minimization by simplex method require values of the objective function. Since we have only differential equation for the conversion and yields, the value of the objective function can be determined only after solving the equations.

The set of differential equations can be solved with the given initial conditions by the 4<sup>th</sup>-order Runge Kutta method.

Consider a set of 'N' differential equations

$$\begin{aligned}
 \frac{dy_1}{dt} &= f_1(t, \bar{y}) \\
 \frac{dy_2}{dt} &= f_2(t, \bar{y}) \\
 &\vdots \\
 \frac{dy_J}{dt} &= f_J(t, \bar{y}) \\
 &\vdots \\
 \frac{dy_N}{dt} &= f_N(t, \bar{y})
 \end{aligned} \tag{3.2}$$

with initial condition  $\bar{y} = 0$  at  $t = 0$

where  $\bar{y} = (y_1, y_2, \dots, y_J, \dots, y_N)$

The 4<sup>th</sup>-order Runge Kutta method gives the values of various functions  $y_1, y_2, \dots, y_N$  at  $(n+1)^{th}$  point when values of these

functions at  $n^{\text{th}}$  point is known. The solution is given by (3.3)

$$Y_{J,n+1} = Y_{J,n} + \frac{h}{6} (k_{J,1} + 2 k_{J,2} + k_{J,3} + k_{J,4}) \quad (3.3)$$

$$J = 1, \dots, N$$

where

$Y_{J,n+1}$  : Value of function  $y_J$  at  $(n+1)^{\text{th}}$  point

$Y_{J,n}$  : Value of function  $y_J$  at  $n^{\text{th}}$  point

$$k_{J,1} = f_J(t_n ; y_{1,n} ; y_{2,n} ; \dots y_{N,n})$$

$$J = 1, \dots, N$$

$$k_{J,2} = f_J(t_n + \frac{h}{2} ; y_{1,n} + \frac{h}{2} k_{11} ; y_{2,n} + \frac{h}{2} k_{21} ; \dots ; y_{N,n} + \frac{h}{2} k_{N,1})$$

$$k_{J,3} = f_J(t_n + \frac{h}{2} ; y_{1,n} + \frac{h}{2} k_{12} ; y_{2,n} + \frac{h}{2} k_{22} ; \dots ; y_{N,n} + \frac{h}{2} k_{N,2})$$

$$k_{J,4} = f_J(t_n + h ; y_{1,n} + h k_{1,3} ; y_{2,n} + h k_{23} ; \dots ; y_{N,n} + h k_{N,3})$$

$$J = 1, 2, \dots, N$$

$h$  is the step size

The flow chart describing the process of parameter estimation is shown in Fig. 3.1.

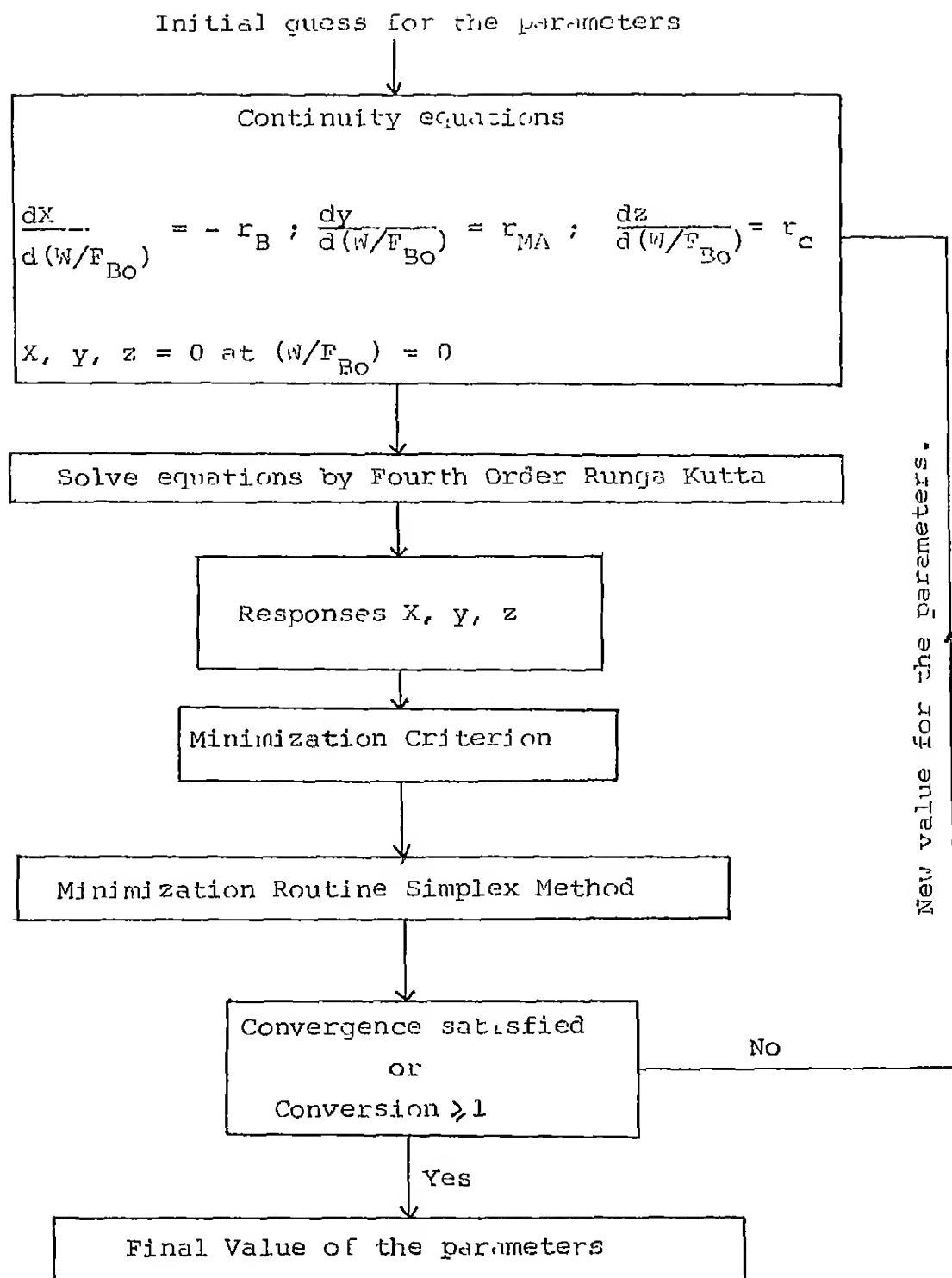


Fig. 3.1. Flow Chart for Parameter Estimation.



### 3.4 SOME OTHER ASPECTS

From physical considerations, it is clear that the conversion of Butane in the reactor can not exceed unity. This factor is important and has been taken into account while determining the parameters.

After each iteration in the minimization process, a new set of parameters is generated. The conversion and yield corresponding to this set of the parameters is obtained by solving the continuity equation using Runge Kutta method. If conversion is found to be greater than one, the minimization is stopped and the value of parameters at that iteration is taken as the final values even if it does not satisfy the convergence criterion.

If the conversion is  $< 1$  and the convergence criterion is not satisfied then the iterative process is repeated.

The computer programme for parameter estimation has been given in Appendix 3.

## CHAPTER 4

### RESULTS AND DISCUSSION

The aim of the present study was to model the selective oxidation of n-butane to maleic anhydride using Gopichand's experimental data (Appendix 1). A general model based on redox mechanism has been proposed by Gopichand (1). This has been slightly modified taking into account the orders of the elementary reactions in the proposed model. This model is given by Equation (2.20) to (2.22); (2.34) to (2.36) and (2.22a). The same equations apply to Gopichand's model except that in Gopichand's model, the orders of reactions m, n, r, s are all equal to unity. In a third model viz., Centi's Model (4), the rate expressions for the productions maleic anhydride,  $\text{CO}_2$  and rate of consumption of n-butane are given by Equations (2.38) to (2.40) in place of (2.34) to (2.36). The results obtained with different models are discussed in the following sections. Parameters involved in this model as well as in the other model proposed by Gopichand (1)

and Centi..et. al (4) have been estimated using sequential simplex method.

#### 4.1 STARTING SIMPLICES FOR PARAMETER ESTIMATION

For the general model as well as Gopichand's model, the starting simplices at various temperatures (350°C, 375°C and 400°C) are given in Tables 1, 2 and 3 respectively. For Centi's model, the starting simplex is given in Table 4.

#### 4.2 GOPICHAND'S MODEL

The values of the intrinsic parameter at different temperatures using Gopichand's model are given in Table 5. The values of all the parameter were found to be positive. The rate constants are plotted in the form of Arrhenius plots, which are given in Fig. 4.1. The activation energies are given in Table 5. The activation energies for  $k_2$ , and  $k_4$  are rather low. This may be due to the nature of data (integral) used, as well as the uncertainties associated with nonlinear estimation. On the average each parameter estimation at a given temperature for a given model took approximately 30-40 min. on PC - XT.

### 4.3 GENERAL MODEL INVOLVING ORDEPS

While estimating parameters the orders 'm' and 'n' have always been taken as one and zero respectively. Also, four combinations of 'r' and 's' have been used. The value of 'r' and 's' were taken as 0.5 or 0.25.

The value of kinetic parameters for various combinations are given in Table 6 to 9.\*

From Table 6 and 7 it can be observed that by changing 's' from 0.5 to 0.25 and keeping 'r' equal to 0.5, the value of parameters did not change. Also from Tables 8 and 9, the value of parameters remain unchanged by changing 's' from 0.5 to 0.25 while keeping 'r' as constant and equal to 0.25.

These observations lead to the conclusion that the kinetic parameters were not much influenced by the order 's'.

The rate constants have been plotted in the form of Arrhenius plots ( $\ln k$  vs  $\frac{1}{T}$ ) and these plots are shown in Figures 4.2 and 4.3. The activation energies  $E_2$  and  $E_4$  are relatively small.

\* In general, the value of rate constant should increase with temperature. However in table 5-9, some spurious values of rate constants were obtained, which are physically not possible. Better data as well as better estimation techniques are desirable.

#### 4.4 CENTI'S MODEL

The values of kinetic parameters at various temperatures are given in Table 10. A plot of  $\ln k$  vs  $\frac{1}{T}$  is given in Fig. 4.4. The activation energy corresponding to various parameters is of the order of 10 kcal/mol which is very small. So it can be concluded that Gopichand's data do not fit well with the Centi's model.

#### 4.5 CONCLUSIONS

From the above discussion it can be concluded that Gopichand's data best fit in the redox model. The centi's model based on Langmuir-adsorption concept is found to be not much useful.

The activation energies as well as R.S.S. values are comparable in the Gopichand's model and general redox model. So from these data it is not possible to discriminate among these two models.

Table 1

Initial Simplex Corresponding to Temperature 350 °C for Redox Model

$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
1.31	0.07	125.34	0.43	116.43
5.92	0.03	134.54	0.39	115.60
2.54	0.63	295.54	0.75	135.65
4.64	0.05	165.84	0.32	123.55
1.04	0.04	145.84	0.63	164.93
2.00	0.05	234.54	0.58	129.04

Table 2

Initial Simplex Corresponding to Temperature 375°C for  
Redox Model

$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
0.1357	0.9439	5.2439	0.3268	21.1234
0.3542	0.0456	7.4328	0.3216	29.4231
0.1543	0.2356	9.8065	0.3218	34.5264
0.2467	0.5086	7.4321	0.5436	28.4356
0.4684	0.0454	5.4728	0.7216	30.4231
0.3487	0.9643	7.5670	0.6742	36.1247

Table 3

Initial Simplex Corresponding to Temperature 400° C for  
Redox Model

$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
0.03	0.04	0.56	0.54	8.97
0.43	0.03	0.34	0.87	3.65
0.32	0.02	0.54	0.21	4.65
0.05	0.04	0.54	0.32	1.54
0.78	0.34	0.09	0.43	10.02
0.45	0.94	0.03	0.54	4.75



Table 4

Initial Simplex for Centu's Model ( All Temperatures )

$k_1$	$k_B$	$k_2$	$k_3$	a	b	$\bar{a}$	$\bar{a}$
0.1357	0.9430	5.2439	0.3268	0.1234	0.6345	1.4321	0.4567
0.3542	0.0456	7.4328	0.3216	0.4231	0.4536	3.4321	1.3245
0.1543	0.2356	9.8065	0.3218	0.5264	0.5463	1.6452	0.5674
0.2467	0.5086	7.4321	0.5436	0.4356	0.2745	2.6453	0.6453
0.4684	0.0454	5.4728	0.7216	0.4231	0.3254	1.9645	1.7645
0.3487	0.9643	7.5670	0.6742	0.1247	0.2343	4.6754	0.6573
0.1254	0.6573	4.6734	0.3452	0.2342	0.4536	2.5438	1.8765
0.3425	0.5463	3.6543	0.1232	0.6545	0.7564	3.5436	0.8750
0.6457	0.3452	2.6453	0.6453	0.8745	0.3452	3.0978	0.4536

Table 5

Kinetic Parameters for Gopichand's Model

Temperature Parameters (Intrinsic Rate Constants)	350°C	375°C	400°C	Activation Energy kcal/mol
$k_1$	0.6444	0.6426	3.906	27.82
$k_2$	0.1483	0.3600	0.2192	7.68
$k_3$	0.0799	0.9390	36.2074	98.70
$k_4$	0.1555	0.1671	0.2056	4.44
$k_5$	0.1790	21.4600	139.7	57.16
R.S.S.	0.06223	0.0218	33.8738	
$\sigma^2 = \frac{R.S.S.}{n-k}$ **	$4.1486 \times 10^{-3}$	$1.4533 \times 10^{-3}$	2.2583	

\*\* n = number of experimental data = 20

k = number of parameter = 5

Table 6

Kinetic Parameters for General Redox Model

(orders  $r = 0.5$ ,  $s = 0.5$ ,  $m = 1.0$ ,  $n = 0$ )

Temperature Parameters	350 °C	375 °C	400 °C	Activation Energy kcal/mol
$k_1$	0.3480	0.2057	3.4320	34.38
$k_2$	0.2780	0.7570	0.7657	17.46
$k_3$	0.3120	7.446	324.50	113.03
$k_4$	0.5400	0.5046	0.7008	3.90
$k_5$	5.7860	30.1900	109.90	48.46
R.S.S.	2.0267	1.1828	0.6539	
$\sigma^2 = \frac{R.S.S.}{n - k}$	0.1351	0.0788	0.0436	

Table 7

Kinetic Parameters for General Redox Model

(orders  $r = 0.5$ ,  $s = 0.25$ ,  $m = 1.0$ ,  $n = 0$ )

Temperature Parameters	350°C	375°C	400°C
$k_1$	0.3480	0.2057	3.432
$k_2$	0.2780	0.7570	0.7657
$k_3$	0.3120	7.446	324.5
$k_4$	0.5400	0.5046	0.7008
$k_5$	5.7860	30.19	109.9
R.S.S.	2.0267	1.4770	0.6539
$\sigma^2 = \frac{R.S.S.}{n - k}$	0.1351	0.0985	0.0436

Table 8

Kinetic Parameters for General Redox Model

(orders  $r = 0.25$ ,  $s = 0.5$ ,  $m = 1.0$ ,  $n = 0$ )

Temperature	350 °C	375 °C	400 °C
Parameters			
$k_1$	0.3480	0.3145	2.201
$k_2$	0.2780	0.3599	0.1778
$k_3$	0.3120	7.5420	193.0
$k_4$	0.5400	0.5166	0.5712
$k_5$	5.786	31.7900	134.20
R.S.S.	2.0267	1.3996	0.9952
$\sigma^2 = \frac{R.S.S.}{n - k}$	0.1351	0.0933	0.0663

Table 9

Kinetic Parameters for General Redox Model

(orders  $r = 0.25$ ,  $s = 0.25$ ,  $m = 1.0$ ,  $n = 0$ )

Temperature Parameters	350 °C	375 °C	400 °C	Activation Energy kcal/mol
$k_1$	0.3760	0.3145	2.201	29.42
$k_2$	0.2760	0.3599	0.6778	14.35
$k_3$	0.3520	7.5420	193.00	102.95
$k_4$	0.4080	0.5166	0.5712	5.62
$k_5$	5.9860	31.7900	134.20	51.05
R.S.S.	1.9099	1.5137	0.9952	
$\sigma^2 = \frac{R.S.S.}{n-k}$	0.1273	1.0091	0.0663	

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Table 10

Kinetic Parameters for Centi's Model

Temperature Parameters	350° C	375° C	400° C
$k_1$	0.7466	0.5924	0.9470
$k_B$	0.7467	0.8833	0.5958
$k_2$	1.3240	3.1250	2.7170
$k_3$	1.0460	0.9169	1.7281
a	0.4270	0.3167	0.5138
b	0.0735	0.0073	0.1968
c	4.1820	4.7060	4.2190
d	1.2200	1.0500	1.3800
R.S.S.	2.1526	3.8349	6.8646
$\sigma^2 = \frac{R.S.S.}{n - k}$	0.1794	0.3196	0.5721

Activation Energy

$$E_1 = 3.25 \text{ kcal/mol}$$

$$E_2 = 12.66 \text{ kcal/mol}$$

$$E_3 = 7.51 \text{ kcal/mol}$$

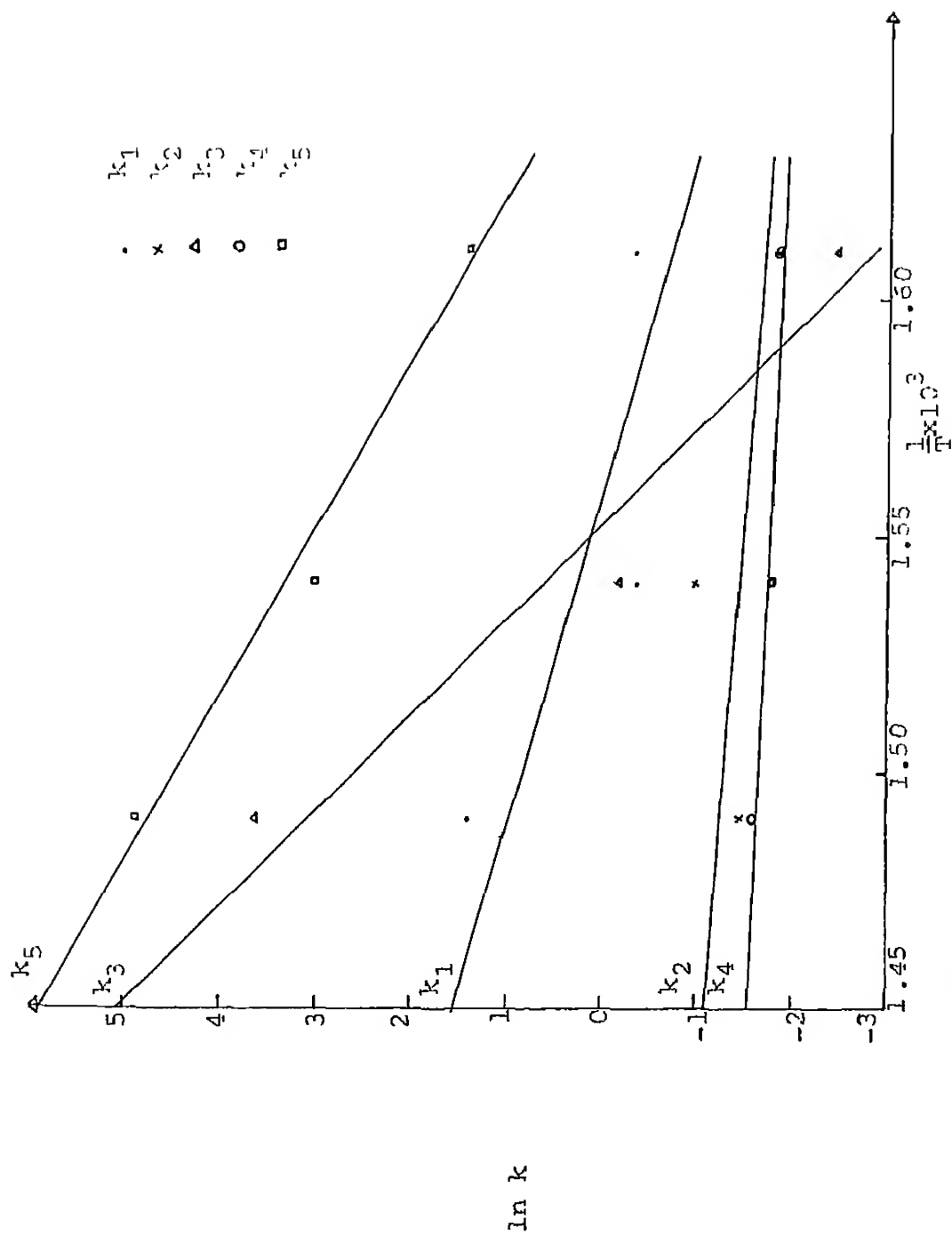


Fig. 4.1. Arrhenius Plot for Rate Constant.  
Redox Model (Gorichand's Model).



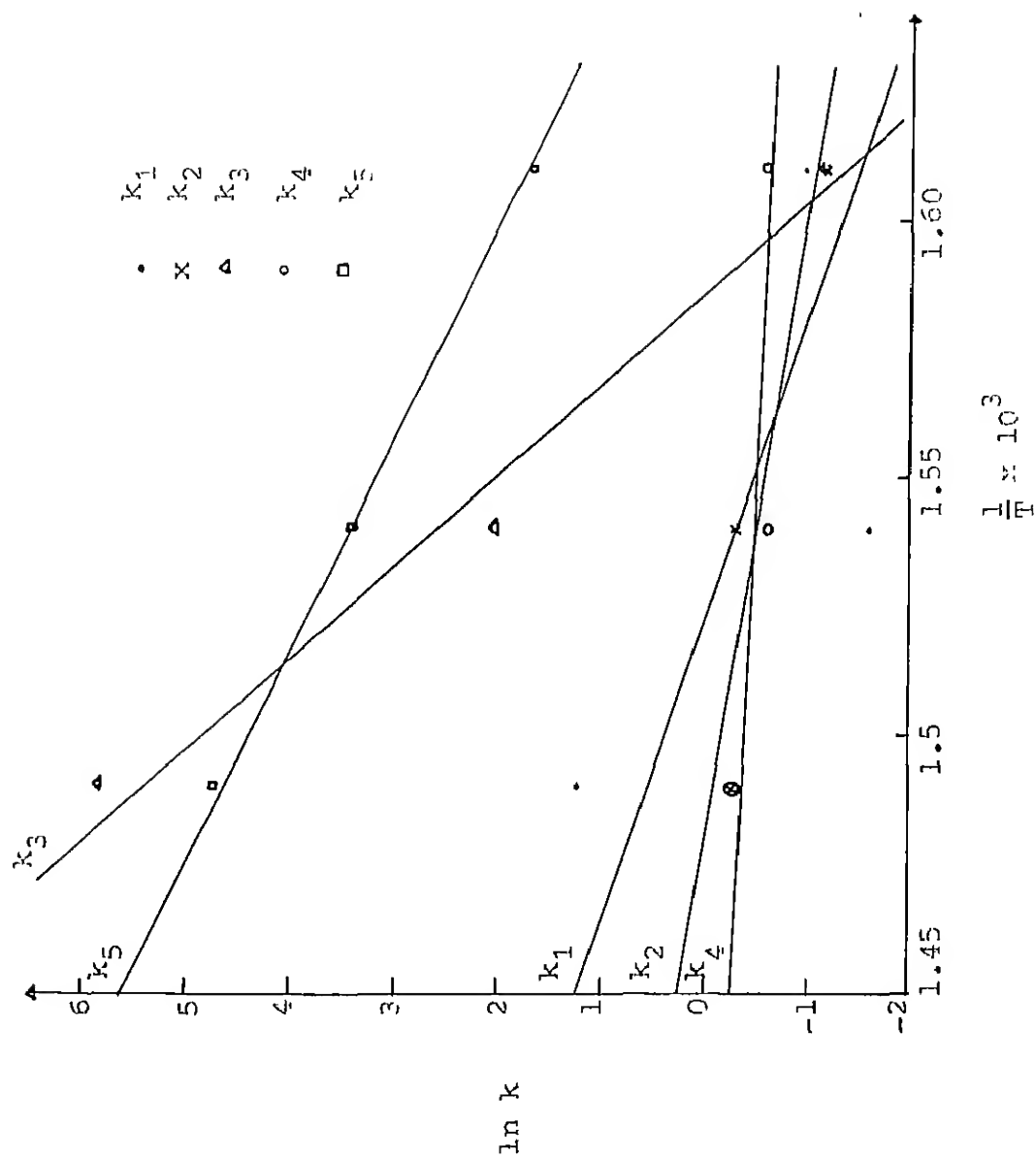


Fig. 4.2. Arrhenius Plot for Rate Constant.  
General Redox Model (using  $r = 0.5$ ,  
 $s = 0.5$ ,  $m = 1.0$ ,  $n = 0$ ).

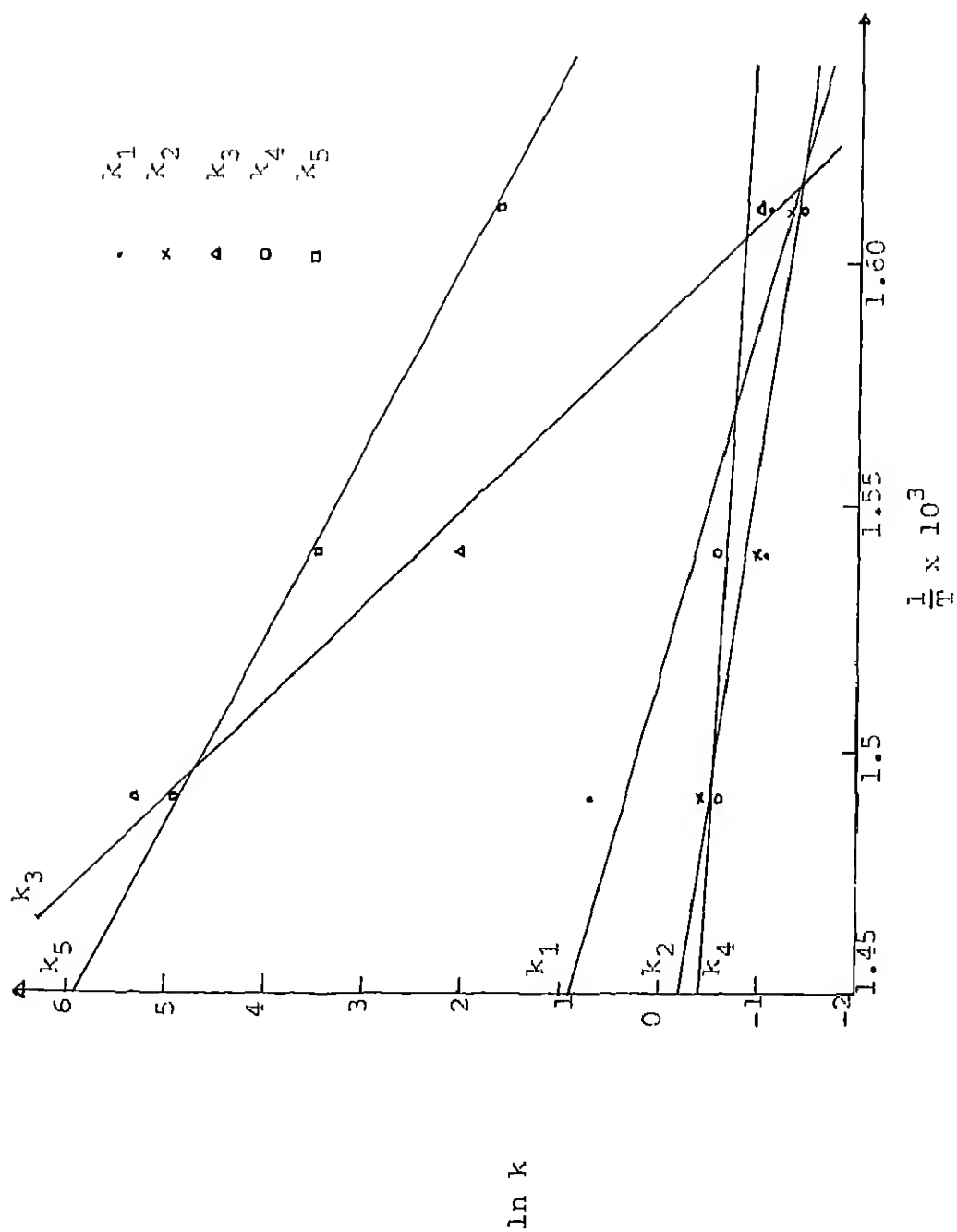


Fig. 4.3. Arrhenius Plot for Rate.  
General Redox Model (using  $r = 0.25$ ,  
 $s = 0.25$ ,  $m = 1.0$ ,  $n = 0$ ).

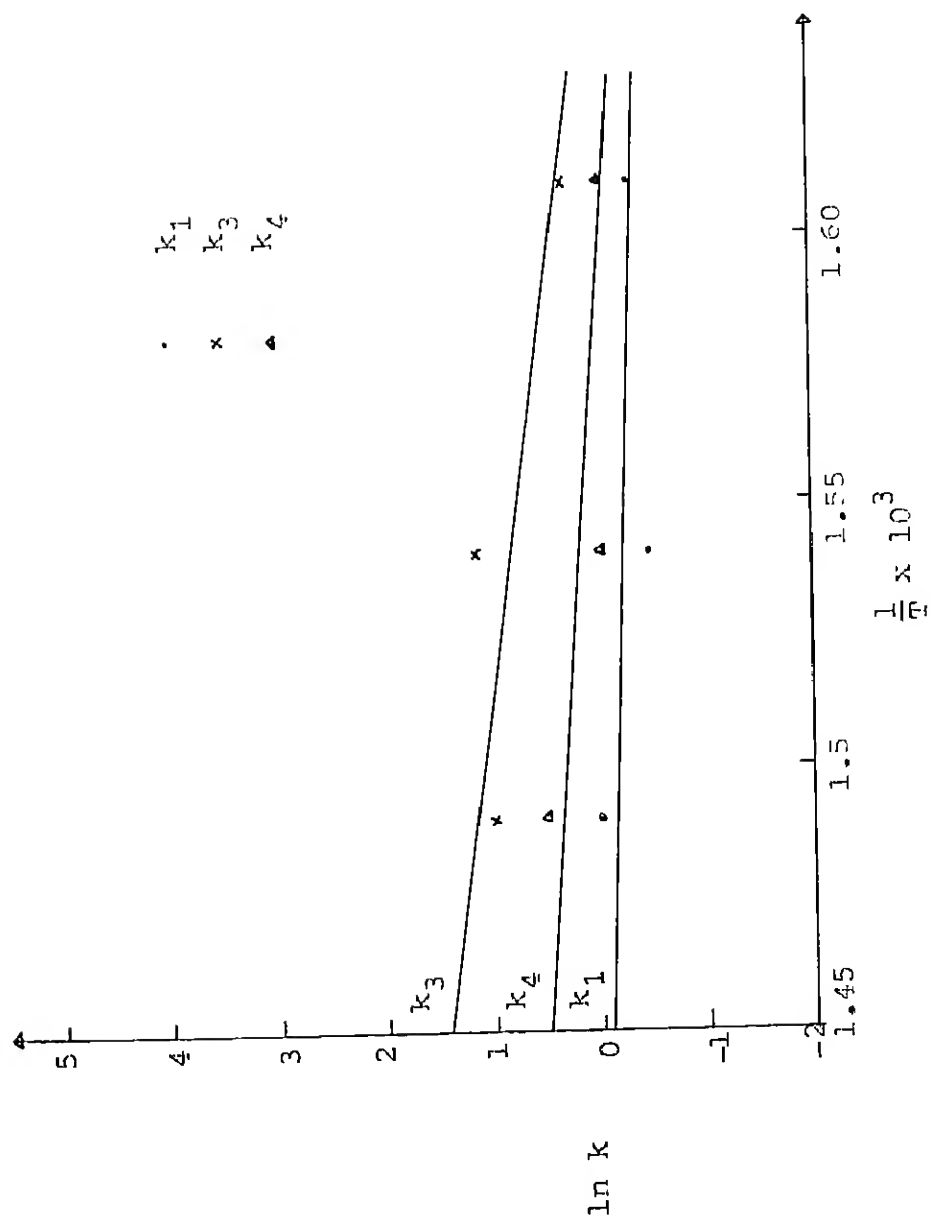


Fig. 4.4. Arrhenius Plot for Rate Constant.  
Centl's Model.

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APPENDIX 1Table 11

Experimental Data at Temperature 350°C

$\frac{W}{F}_{Bo}$	PBO* atm.	Conversion of B	Yield of MA	Yield of C
3.0	0.006	0.4317	0.1205	0.3166
4.5	0.006	0.5317	0.1558	0.3763
6.0	0.006	0.6267	0.1933	0.4329
7.5	0.006	0.6800	0.2183	0.4625
9.0	0.006	0.7350	0.2450	0.4917
3.0	0.008	0.4800	0.1095	0.3706
4.5	0.008	0.6113	0.1500	0.4613
6.0	0.008	0.6725	0.1725	0.5013
7.5	0.008	0.7388	0.1987	0.5396
9.0	0.008	0.7863	0.2200	0.5672
3.0	0.010	0.5330	0.1040	0.4286
4.5	0.010	0.6450	0.1350	0.5110
6.0	0.010	0.7190	0.1580	0.5605
7.5	0.010	0.7710	0.1780	0.5940
9.0	0.010	0.8250	0.2000	0.6250
3.0	0.012	0.6292	0.1100	0.5185
4.5	0.012	0.6875	0.1258	0.5619
6.0	0.012	0.7682	0.1500	0.6146
7.5	0.012	0.8200	0.1683	0.6500
9.0	0.012	0.8392	0.1767	0.6625

\* PBO is partial pressure of butane in feed stream.

Table 12

Experimental Data at Temperature 375 °C

$\frac{W}{F}_{Bo}$	PBO* atm.	Conversion of B.	Yield of MA	Yield of C
3.0	0.006	0.2250	0.1328	0.0928
4.5	0.006	0.3017	0.1800	0.1212
6.0	0.006	0.3883	0.2367	0.1513
7.5	0.006	0.4450	0.2733	0.1704
9.0	0.006	0.5083	0.3183	0.1906
3.0	0.008	0.2413	0.1250	0.1159
4.5	0.008	0.3488	0.1850	0.1634
6.0	0.008	0.4088	0.2200	0.1884
7.5	0.008	0.4863	0.2675	0.2186
9.0	0.008	0.5500	0.3075	0.2422
3.0	0.010	0.2650	0.1230	0.1420
4.5	0.010	0.3610	0.1710	0.1895
6.0	0.010	0.4400	0.2140	0.2265
7.5	0.010	0.5070	0.2500	0.2560
9.0	0.010	0.5880	0.2980	0.2898
3.0	0.012	0.3300	0.1400	0.1900
4.5	0.012	0.3883	0.1675	0.2210
6.0	0.012	0.4842	0.2142	0.2697
7.5	0.012	0.5608	0.2542	0.3065
9.0	0.012	0.5933	0.2717	0.3196

\* PBO is partial pressure of butane in feed stream.

Table 13

Experimental Data at Temperature 400°C

$\frac{W}{F_{Bo}}$	PBO *	Conversion of B	Yield of MA	Yield of C
3.0	0.006	0.1433	0.1223	0.0215
4.5	0.006	0.1983	0.1667	0.0316
6.0	0.006	0.2667	0.2217	0.0451
7.5	0.006	0.3133	0.2567	0.0550
9.0	0.006	0.3700	0.3017	0.0683
3.0	0.008	0.1433	0.1139	0.0268
4.5	0.008	0.2150	0.1712	0.0441
6.0	0.008	0.2600	0.2050	0.0559
7.5	0.008	0.3238	0.2500	0.0728
9.0	0.008	0.3813	0.2900	0.0900
3.0	0.010	0.1440	0.1110	0.0329
4.5	0.010	0.2070	0.1570	0.0504
6.0	0.010	0.2650	0.1970	0.0683
7.5	0.010	0.3190	0.2330	0.0855
9.0	0.010	0.3920	0.2800	0.1115
3.0	0.012	0.1733	0.1267	0.0470
4.5	0.012	0.2117	0.1517	0.0593
6.0	0.012	0.2817	0.1975	0.0839
7.5	0.012	0.3458	0.2367	0.1087
9.0	0.012	0.3750	0.2542	0.1207

\* PBO is partial pressure of butane in feed stream.



## APPENDIX 2

### SIMPLEX METHOD

In an  $n$  dimensional space, a geometric figure formed by a set of  $(n+1)$  points is called a simplex. In the simplex method the values of the objective function at the  $(n+1)$  vertices is compared and the simplex is moved to an optimum point during the iterative process. The movement of simplex involve three operations reflection, contraction and expansion, the details of which are given by Rao (8) and are as follows:

#### (1) REFLECTION

If  $X_h$  is the vertex corresponding to the highest value of the objective function among the vertices of a simplex, one can expect the point  $X_r$  obtained by reflecting the point  $X_h$  in the opposite face to have the smallest value. If this is the case, then one can construct a new simplex by rejecting the point  $X_h$  from the simplex and including the new point  $X_r$ .

This procedure is shown in the Fig. A(1a). The points  $X_1, X_2, X_3$  form the original simplex, and the point  $X_1, X_2$  and  $X_r$  form the new one. Similarly in Fig. A(1b), the original simplex

is given by points  $X_1, X_2, X_3$  and  $X_4$  and the new one by  $X_1, X_2, X_3$  and  $X_r$ . Again one can construct a new simplex from the present one by rejecting the vertex corresponding to the highest functional value.

Since the direction of movement of the simplex is always away from the worst result, we will be moving in a favourable direction. If the objective function does not have step valleys, repetitive application of the reflection process leads to a zig-zag path in the general direction of the minimum as shown in Fig. A(2).

Mathematically, the reflected point  $X_r$  is given by

$$X_r = (1 + \alpha) X_o - \alpha X_h \quad (1)$$

Where  $X_h$  is the vertex corresponding to the maximum function value i.e.

$$f(X_h) = \max_{i=1 \text{ to } (n+1)} f(X_i) ;$$

$X_o$  is the centroid of all the points  $X_i$  except  $i = n$  and given by

$$X_o = \frac{1}{n} \sum_{\substack{i=1 \\ i \neq h}}^{n+1} (X_i)$$

and  $\alpha > 0$  is the reflection coefficient defined as

$$\alpha = \frac{\text{distance between } X_r \text{ and } X_o}{\text{distance between } X_h \text{ and } X_o}$$

Thus  $X_r$  will lie on the line joining  $X_h$  and  $X_o$  on the far side of  $X_o$  from  $X_h$  with  $|X_r - X_o| = \alpha |X_h - X_o|$ . If  $f(X_i)$  lies between  $f(X_h)$  and  $f(X_1)$  where  $X_1$  corresponds to the minimum function value i.e.,

$$f(X_1) = \min_{i=1 \text{ to } (n+1)} f(X_i)$$

$X_h$  is replaced by  $X_r$  and a new simplex is started.

If we use only the reflection process for finding the minimum, we may encounter certain difficulties in some cases. For example if one of the simplexes (triangle in two dimensions) straddles a valley as shown in Fig.A(3) and if the reflected point  $X_r$  happen to have an objective function value equal to the of the point  $X_h$ , we will enter into a closed cycle of operations. Thus if  $X_2$  is the worst point in the simplex defined by the vertices  $X_1$ ,  $X_2$  and  $X_3$ , the reflection process gives a new simplex with vertices  $X_1$ ,  $X_3$  and  $X_r$ . Again  $X_r$  has the highest

functional value out of the vertices  $X_1$ ,  $X_3$  and  $X_r$ , we obtain old simplex itself by using the reflection process. Thus the optimization process is stranded over the valley and there is no way of moving towards the optimum point. This trouble can be overcome by making a rule that no return can be made to points which have just been

Whenever such situation is encountered, we reject the vertex corresponding to the second worst value instead of the vertex corresponding to the worst function value. This method, in general, leads the process to continue towards the region of the desired minimum. However the final simplex may again straddle the minimum, or it may lie within a distance of the order of its own size from the minimum. In such cases, it may not be possible to obtain a new simplex with vertices closer to the minimum compared to those of the previous simplex, and the pattern may lead to a cycle process as shown in Fig. A(4).

In the above, successive simplexes formed from the simplex 123, 234, 245, 456, 467, 478, 348, ... which can be seen to be forming a cycle process. Whenever this type of cycling is observed, one can take the vertex that is occurring in every simplex (point 4 in fig.) as the best approximation to the optimum point. If more accuracy is desired, the simplex has to be contracted or reduced in size.

(ii) EXPANSION

If a reflection process gives a point  $X_r$  for which  $f(X_r) < f(X_1)$  i.e. if the reflection produces a new minimum, one can generally expect to decrease the function value further by moving along the direction  $X_0$  and  $X_r$ . Hence we expand  $X_r$  to  $X_e$  by the relation.

$$X_e = \gamma X_r + (1 - \gamma) X_0 \quad (2)$$

$\gamma$ , is called expansion coefficient defined as

$$\gamma = \frac{\text{distance between } X_e \text{ and } X_0}{\text{distance between } X_r \text{ and } X_0} > 1$$

if  $f(X_e) < f(X_1)$ , we replace the point  $X_h$  by  $X_e$  and restart the process of reflection. On the other hand if  $f(X_e) > f(X_1)$  it means that the expansion process is not successful and hence we replace the point  $X_h$  by  $X_r$  and start the reflection process again.

(iii) CONTRACTION

If the reflection process gives a point  $X_r$  for which  $f(X_r) > f(X_1)$  for all  $i$  excepting  $i = h$  and  $f(X_r) < f(X_h)$ , then we replace the point  $X_h$  by  $X_r$ . Thus the new  $X_h$  will be  $X_r$ . In this case the simplex is contracted as follows:

$$X_c = \beta X_h + (1 - \beta) X_0 \quad (3)$$

Where  $\beta$  is called contraction coefficient  $0 \leq \beta \leq 1$  and is defined as

$$\beta = \frac{\text{distance between } X_c \text{ and } X_o}{\text{distance between } X_h \text{ and } X_o}$$

if  $f(X_r) > f(X_h)$ , use Equation (3) without changing the previous point  $X_h$ . If the contraction process produces a point  $X_c$  for which  $f(X_c) < \min [f(X_h), f(X_r)]$ , we replace the point  $X_h$  in  $X_1, X_2, \dots, X_{n+1}$  by  $X_c$  and proceed with the reflection process again. On the other hand if  $f(X_c) \geq \min [f(X_h), f(X_r)]$ , the contraction process will be a failure and in this case, we replace all  $X_i$  by  $(X_i + X_1)/2$  and restart the reflection process.

The method is assumed to have converged whenever the standard deviation of the function at the  $(n+1)$  vertices of the current simplex is smaller than some prescribed small quantity i.e.

$$Q = \left[ \sum_{i=1}^{n+1} \frac{f(X_i) - f(X_o)}{n+1} \right]^{\frac{1}{2}}$$

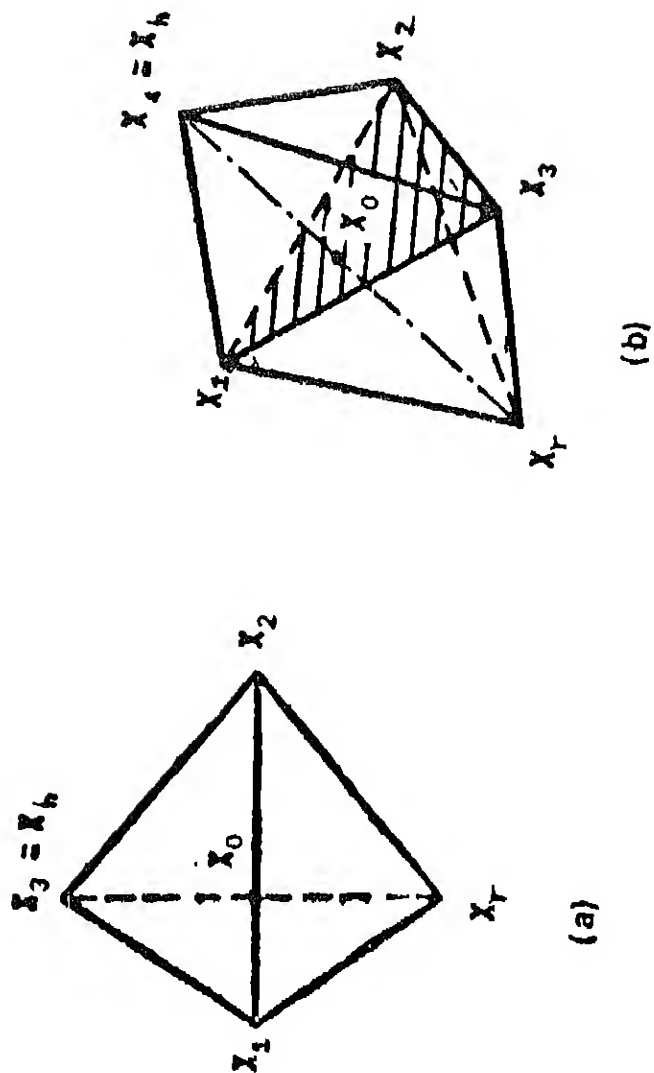


Fig. A(4) Reflection

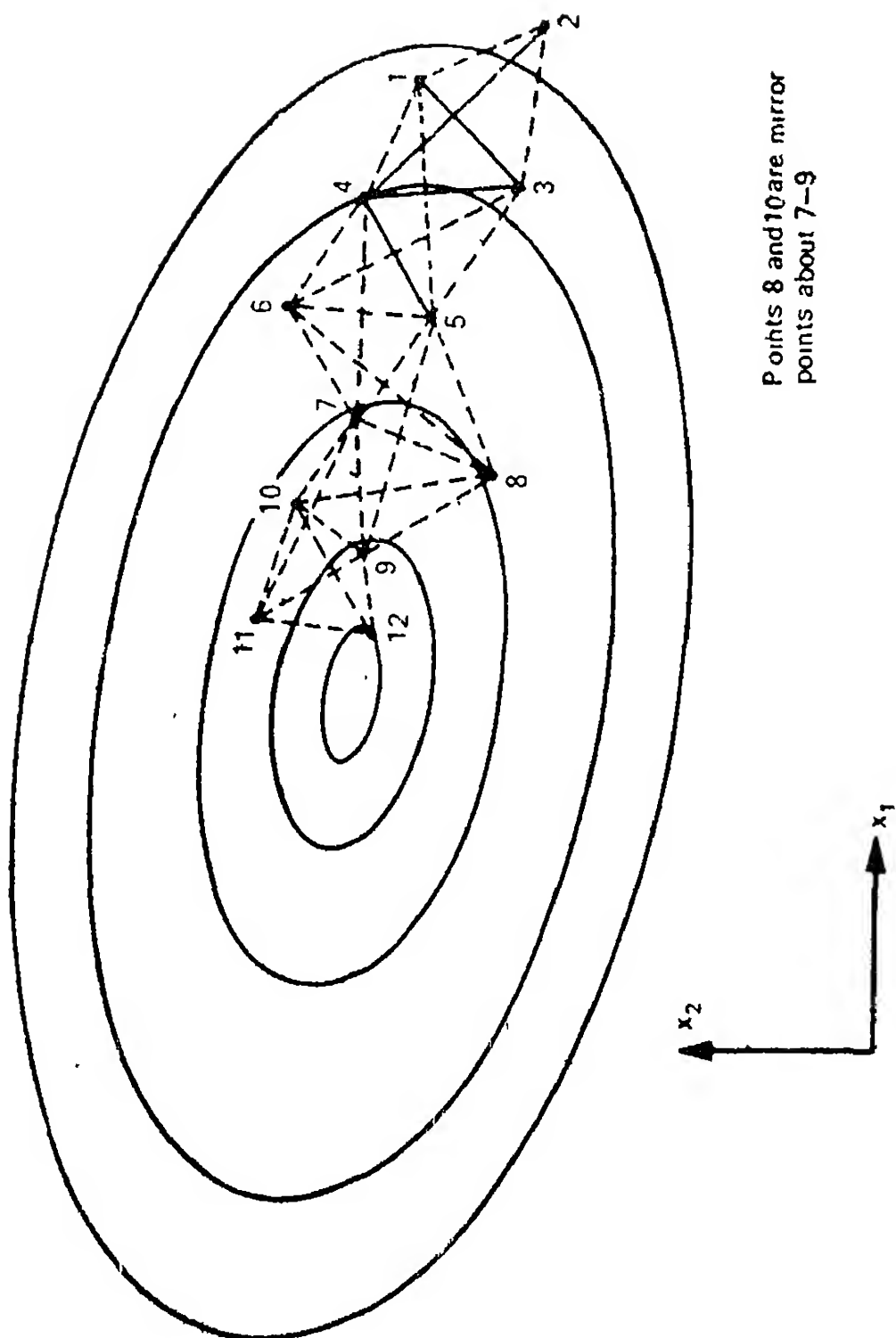


Fig. A(z). Progress of reflection process.



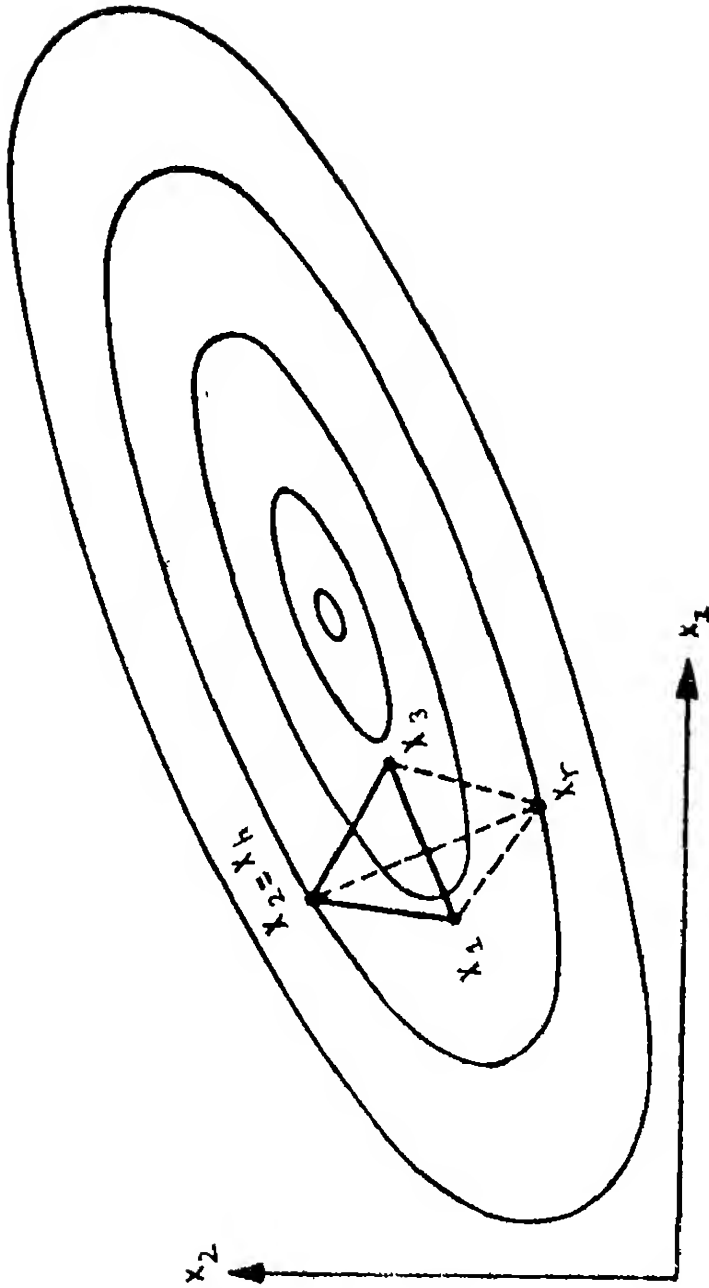


Fig. A(3) Reflection process not leading to a new simplex.

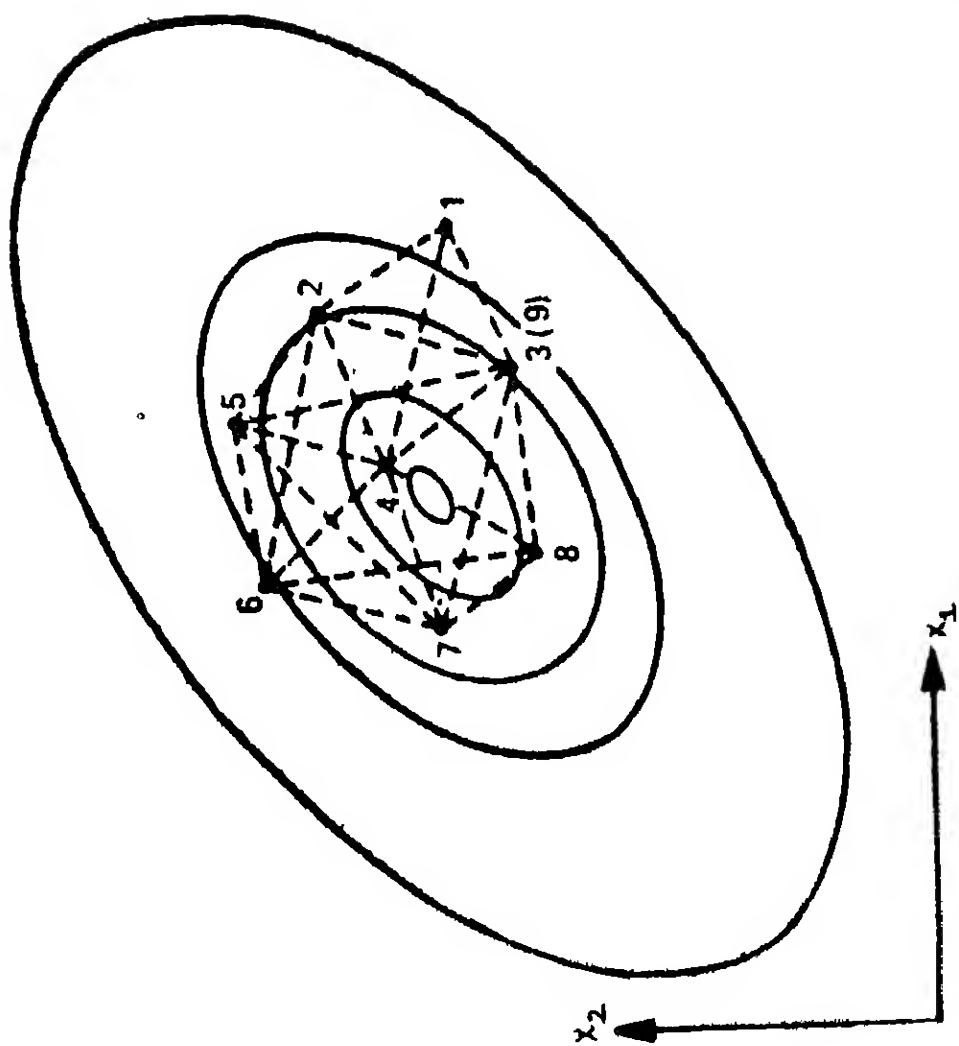


Fig.A(4) Reflection process leading to a cyclic process.

# APPENDIX - 3

## PARAMETER ESTIMATION

THIS PROGRAMME SOLVE THE CONTINUITY EQUATIONS USING FOURTH ORDER RUNGA KUTTA METHOD AND USES SIMPLEX METHOD TO MINIMIZE THE LEAST SQUARE FUNCTION TO ESTIMATE THE PARAMETERS.

```
REAL X(20),PBO(20),YM(20,3)
REAL P(6,5),Y(6),YI(3),K(5),YC(20,3),XC(20),KC(5),PAR(6)
INTEGER M,NDIM,L
REAL H,MAX,SUMP
```

'PBO' IS PARTIAL PRESSURE OF BUTANE IN FEED STREAM.  
 'YM' IS A MATRIX OF CONVERSION AND YIELDS.  
 X=W/FO WHERE 'W' IS WEIGHT OF CATALYST, 'FO' IS FLOW RATE OF FEED STREAM.  
 'P' IS A MATRIX OF INITIAL PARAMETERS.  
 'Y' IS A VECTOR CONTAINING VALUE OF FUNCTION CORRESPONDING TO INITIAL PARAMETERS.  
 'YC' IS A VECTOR CONTAINING INITIAL CONDITIONS TO SOLVE THE CONTINUITY EQUATIONS.

```
OPEN(UNIT=5,FILE='FOR5.DAT')
OPEN(UNIT=6,FILE='FOR6.DAT')
OPEN(UNIT=21,FILE='FOR21.DAT')
M=20
NDIM=5
MP=(NDIM+1)
NP=NDIM
FTOL=0.01
DO 20 I=1,M
  READ(5,*) X(I),PBO(I),(YM(I,J),J=1,3)
CONTINUE
DO 30 I=1,(NDIM+1)
  READ(6,*)(P(I,J),J=1,NDIM)
CONTINUE
DO 50 I=1,6
  DO 40 J=1,5
    K(J)=P(I,J)
  CONTINUE
  CALL RUNGA(K,YC,XC)
  DO 10 J=1,20
    CONTINUE
  Y(I)=FUNK(YC,YM)
CONTINUE
WRITE(21,996)
CALL AMOEBA(P,Y,MP,NP,NDIM,FTOL,ITER,YM)
WRITE(21,996)
DO 60 J=1,6
  WRITE(21,*)(P(I,J),J=1,5)
WRITE(21,998) Y(I)
```

```

C 60      CONTINUE
          MAX=Y(1)
          DO 100 J=2,6
            IF(Y(I).GT.MAX) MAX=Y(I)
100      CONTINUE
          DO 200 J=1,6
            IF(Y(J).EQ.MAX) L=J
200      CONTINUE
          DO 300 I=1,5
            SUMP=0
            DO 400 J=1,6
              IF(J.EQ.L)GO TO 400
              SUMP=SUMP+P(J,I)
400      CONTINUE
            PAR(I)=(SUMP/5.0)
300      CONTINUE
          WRITE(21,1000)
          DO 500 I=1,5
            WRITE(21,998) PAR(I)
500      CONTINUE
          DO 600 I=1,5
            KC(I)=PAR(I)
600      CONTINUE
          CALL RUNGA(KC,YC,XC)
          RSS=FUNK(YC,YM)
          WRITE(21,1100)
          WRITE(21,*)RSS
C          WRITE(21,997)ITER
996      FORMAT(1X,'THE MATRIX FROM SUBROUTINE AMOEBA IS')
997      FORMAT(1X,'THE NUMBER OF ITERATION IS=',I3)
998      FORMAT(1X,1PE10.3)
1000     FORMAT(1X,'THE VALUE OF PARAMETERS IS')
1100     FORMAT(1X,'THE RESIDUAL SUM OF SQUARES IS')
1200     FORMAT(1X,'THE VALUE FROM RUNGA CALLED IN MAIN PROGRAM')
          STOP
          END
C          *****
C          SUBPROGRAM TO CALCULATE FUNCTION
          FUNCTION FUNK(YC,YM)
          DIMENSION YC(20,3),YM(20,3)
          SUM=0
          DO 20 I=1,20
            DO 30 J=1,3
              SUM=SUM+(YM(I,J)-YC(I,J))**2
30      CONTINUE
20      CONTINUE
          FUNK=SUM
          RETURN
          END
C          *****
C          SUBPROGRAM TO SOLVE SIMULTANEOUS EQUATIONS
          SUBROUTINE RUNGA(KC,YC,XC)
          DIMENSION YI(3),F(2),YO(2),T(4,2),YC(20,3),XC(20)
          REAL KC(5)

```

```

PBO=0.004
M=1
DO 5 S=1,4
POO=0.208
PBO=(PBO+0.002)
H=0.5
XI=0
YI(1)=0
YJ(2)=0
YI(3)=0
DO 10 I=M,M+4
DO 100 N=1,3
300 XO=XJ
YO(1)=YI(1)
YO(2)=YI(2)
CALL DERIV(KC,YI,F,POO,PBO)
DO 20 J=1,2
20 T(1,J)=F(J)
CONTINUE
XI=XO+(H/2.0)
YI(1)=YO(1)+(H*T(1,1)/2.0)
YI(2)=YO(2)+(H*T(1,2)/2.0)
CALL DERIV(KC,YI,F,POO,PBO)
DO 30 J=1,2
30 T(2,J)=F(J)
CONTINUE
XJ=XO+(H/2.0)
YI(1)=YO(1)+(H*T(2,1)/2.0)
YI(2)=YO(2)+(H*T(2,2)/2.0)
CALL DERIV(KC,YI,F,POO,PBO)
DO 40 J=1,2
40 T(3,J)=F(J)
CONTINUE
XI=XO+H
YI(1)=YO(1)+(H*T(3,1))
YI(2)=YO(2)+(H*T(3,2))
CALL DERIV(KC,YI,F,POO,PBO)
DO 23 J=1,2
23 T(4,J)=F(J)
CONTINUE
DO 24 J=1,2
YI(J)=YO(J)+(T(1,J)+2*T(2,J)+2*T(3,J)+T(4,J))*(H/6.0)
24 CONTINUE
YI(3)=YI(1)-YI(2)
100 CONTINUE
IF(XI.EQ.1.5)GO TO 300
DO 25 J=1,3
25 YC(I,J)=YI(J)
CONTINUE
XC(I)=XI
10 CONTINUE
M=M+5
5 CONTINUE
RETURN
END

```

```

C      *****
C      SUBPROGRAM TO CALCULATE DERIV
      SUBROUTINE DERIV(KC,YI,F,POO,PBO)
      REAL KC(5),F(2),YI(3)
      PB=PBO*(1.0-YI(1))
      PMA=PBO*YI(2)
      PO=POO-3.5*PBO*YI(2)-5.82*PBO*(YI(1)-YI(2))
      F(1)=(KC(1)*PO+KC(3)*PB)/(1+(KC(1)*PO/KC(2)*PB)+
1      (KC(3)*PB/KC(5)*PO)+(KC(4)*PMA/KC(5)*PO))
      F(2)=(KC(1)*PO-KC(4)*PMA)/(1+(KC(1)*PO/KC(2)*PB)+
1      (KC(3)*PB/KC(5)*PO)+(KC(4)*PMA/KC(5)*PO))
      RETURN
      END
C      *****
      SUBROUTINE AMOEBA(P,Y,MP,NP,NDIM,FTOL,ITER,YM)
      PARAMETER (NMAX=20,ALPHA=1.0,BETA=0.5,GAMMA=2.0,ITMAX=500)
      REAL P(MP,NP),Y(MP),PR(NMAX),PRR(NMAX)
1      ,PBAR(NMAX),YC(20,3),YM(20,3),XC(20),S(5)
      MPTS=NDIM+1
      ITER=0
1      ILO=1
      IF(Y(1).GT.Y(2))THEN
          IHI=1
          INHI=2
      ELSE
          IHI=2
          INHI=1
      ENDIF
      DO 11 I=1,MPTS
          IF(Y(I).LT.Y(ILO)) ILO=I
          IF(Y(I).GT.Y(IHI))THEN
              INHI=IHI
              IHI=I
          ELSE IF(Y(I).GT.Y(INHI))THEN
              IF(I.NE.IHI) INHI=I
          ENDIF
11      CONTINUE
      RTOL=2.*ABS(Y(IHI)-Y(ILO))/(ABS(Y(IHI))+ABS(Y(ILO)))
      IF(RTOL.LT.FTOL)RETURN
      IF(ITER.EQ.ITMAX) RETURN
      ITER=ITER+1
      IF(ITER.EQ.1)GO TO 10
      DO 8 I=1,6
          DO 9 J=1,5
              S(J)=P(I,J)
9          CONTINUE
          CALL RUNGA (S,YC,XC)
          DO 90 K=1,20
              IF(YC(K,1).GT.1.0)THEN
                  WRITE(21,2)
2          FORMAT(1X,'CONVERSION EXCEEDS UNITY')
                  RETURN
              ELSE
                  ENDIF

```

```

90      CONTINUE
8       CONTINUE
10      DO 12 J=1,NDIM
        PBAR(J)=0.
12      CONTINUE
        DO 14 I=1,MPTS
          IF(I.NE.IHI)THEN
            DO 13 J=1,NDIM
              PBAR(J)=PBAR(J)+P(I,J)
13          CONTINUE
            ENDIF
14      CONTINUE
        DO 15 J=1,NDIM
          PBAR(J)=PBAR(J)/NDIM
          PR(J)=(1.+ALPHA)*PBAR(J)-ALPHA*P(IHI,J)
15      CONTINUE
C       YPR=FUNK(PR)
        CALL RUNGA(PR,YC,XC)
        YPR=FUNK(YC,YM)
        IF(YPR.LE.Y(ILO))THEN
          DO 16 J=1,NDIM
            PRR(J)=GAMMA*PR(J)+(1.-GAMMA)*PBAR(J)
16      CONTINUE
C       YPRR=FUNK(PRR)
        CALL RUNGA(PRR,YC,XC)
        YPRR=FUNK(YC,YM)
        IF(YPRR.LT.Y(ILO))THEN
          DO 17 J=1,NDIM
            P(IHI,J)=PRR(J)
17      CONTINUE
          Y(IHI)=YPRR
        ELSE
          DO 18 J=1,NDIM
            P(IHI,J)=PR(J)
18      CONTINUE
          Y(IHI)=YPR
        ENDIF
        ELSE IF(YPR.GE.Y(INHI))THEN
          IF(YPR.LT.Y(IHI))THEN
            DO 19 J=1,NDIM
              P(IHI,J)=PR(J)
19      CONTINUE
            Y(IHI)=YPR
          ENDIF
          DO 21 J=1,NDIM
            PRR(J)=BETA*P(IHI,J)+(1.-BETA)*PBAR(J)
21      CONTINUE
C       YPRR=FUNK(PRR)
        CALL RUNGA(PRR,YC,XC)
        YPRR=FUNK(YC,YM)
        IF(YPRR.LT.Y(IHI))THEN
          DO 22 J=1,NDIM
            P(IHI,J)=PRR(J)
22      CONTINUE

```

```

      Y(IHI)=YPRR
    ELSE
      DO 24 I=1,MPTS
        IF(I.NE.ILO)THEN
          DO 23 J=1,NDIM
            PR(J)=0.5*(P(I,J)+P(ILO,J))
            P(I,J)=PR(J)
23          CONTINUE
C          Y(I)=FUNK(PR)
          CALL RUNGA(PR,YC,XC)
          Y(I)=FUNK(YC,YM)
          ENDIF
24        CONTINUE
          ENDIF
        ELSE
          DO 25 J=1,NDIM
            P(IHI,J)=PR(J)
25          CONTINUE
          Y(IHI)=YPRR
          ENDIF
          GO TO 1
100        FORMAT(1X,'THE ITERATION NUMBER=',I3)
200        FORMAT(1X,'THE VALUES FROM RUNGA CORRESPONDING TO PR1')
300        FORMAT(1X,'THE VALUES FROM RUNGA CORRESPONDING TO PRR1')
400        FORMAT(1X,'THE VALUES FROM RUNGA CORRESPONDING TO PR2')
500        FORMAT(1X,'THE VALUES FROM RUNGA CORRESPONDING TO PRR2')
      END
C      *****
C      *****

```



Th  
660.299  
J 78m

A107858

